Chemicals from Coal: The Acetyl Value Stream

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Abstract

Well-established technologies for the conversion of syn-gas can be utilized to manufacture each of the primary materials that constitute the acetyl value chain, i.e., methanol, acetic acid (acetic anhydride) and vinyl acetate. Interest in driving the utilization of syn-gas resources further down the acetyl value chain arises not only from the necessity to efficiently utilize domestic carbon sources but also from issues of global competitiveness. The first-discovered commercializable low-water containing homogeneous catalyst system for the production of acetic acid utilizes a non-noble metal catalyst (nickel). A number of studies, including our own, have indicated that phosphines are important not only to stabilize the catalyst but they also have a substantial effect on the rate of carbonylation. We will discuss a study of this catalyst system that is based upon both kinetic and in-situ monitoring results.

Introduction

Eastman Chemical Company has demonstrated a long-term commitment to the utilization of syngas in the commercial manufacture of acetyl chemicals. Our "Chemicals from Coal" complex practices the carbonylation of methyl acetate to acetic anhydride, a
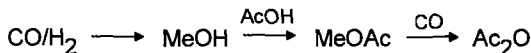
$$CO/H_2 \longrightarrow MeOH \xrightarrow{AcOH} MeOAc \xrightarrow{CO} Ac_2O$$

Figure 1: Eastman's Chemicals from Coal Stream

process utilizing only syngas derived feedstocks. In this facility the synthesis of acetic acid is accomplished by the methanolysis of acetic anhydride. Typically, however, the large-scale production of acetic acid is carried out by the homogeneously catalyzed low-pressure carbonylation of methanol. Commercial facilities currently utilize either a rhodium or iridium based homogeneous catalyst and a methyl iodide promoter. Early attempts to utilize less-expensive nickel catalysts indicated that severe process conditions (pressures as high as 26.7 kPa and temperatures in the range of 250-300°C) were required to achieve reasonable reaction rates. More recently, it was found that the severity of the required process conditions could be considerably reduced by the use of appropriate promoters and the nickel-catalyzed reaction became a viable competitor to other commercial catalyst systems.

The catalyst system for the nickel-catalyzed acetic acid process consists of nickel and molybdenum compounds, an iodide promoter and a phosphine. Under reaction conditions the phosphine exists largely as the phosphonium iodide (adduct with methyl iodide). However, high-pressure infrared studies suggest that substantial quantities of the free phosphine are present and available to act as ligands in the catalytically active metal complex. This is consistent with the notion that the phosphorous component of the catalyst mixture is important in suppressing the formation of the inactive $Ni(CO)_4$ which is present only in trace amounts when the steady-state catalysis is rapid. It also provides an ability to modify the behavior of the catalytic process as changes in the electronic and steric properties of the phosphine are reflected in both the amount of free phosphine present under catalytic conditions and in the nature of the catalytically active species. Indeed, we have been able to observe changes in the rate of catalysis as the nature of the phosphorus promoter changes.

Experimental

The reaction systems described here have been studied by an in situ CIR-FTIR reactor. This equipment and the experimental conditions have been described.[1] Measurement of the rate of various reactions was obtained by monitoring the number of moles of carbon monoxide consumed by the reaction mixture. This was accomplished by either the use of mass-flow control meters or by monitoring the pressure-drop in a surge tank used to supply carbon monoxide to the reaction vessel. In a typical experiment NiI_2 (1.72g), PPh_3 (5.76g), $Mo(CO)_6$ (0.89g), methyl iodide (25.8g), acetic acid (53.5 mL), methanol (53 mL), water (7.3mL) and methyl acetate (11 mL) were loaded into a 300 mL stirred

autoclave constructed from all Hastelloy C components. The autoclave was sealed, purged with CO and then pressurized to 11.3 kPa with CO and the pressure monitored for evidence of leaks. If no leaks were evident the autoclave was vented, stirring begun and 0.9 kPa of H_2 and 4.1 kPa of CO added. After heating to 210°C the total autoclave pressure was increased to 11.3 kPa with carbon monoxide and the pressure maintained by adding additional carbon monoxide as needed. The quantity of carbon monoxide added was recorded at three-minute intervals for a total reaction time of 5 hours. Regression analysis of the slope of the region of steady-state carbon monoxide consumption and a knowledge of the reaction volume charged to the autoclave allowed the calculation of the space-time yield (moles/L-Hr). After the reaction was complete, the autoclave was cooled to room temperature, vented and unloaded. Exact autoclave compositions for the experiments were determined by routine gas chromatographic analysis of the product mixture.

Results and Discussion

A mechanistic scheme that explains the major features of the reaction and is consistent with both the kinetic and in situ CIR-FTIR observations[2] is shown in Figure 2. It suggests that a catalytically active nickel(0) species is available as a result of both a hydrogen enabled reduction from Ni(II) and the delivery of free phosphine ligand from the equilibrium dissociation of the phosphonium salt. The catalytic cycle itself is fairly unremarkable when compared with similar postulated mechanisms for the rhodium catalysts. Methyl iodide is delivered to the catalytic carrier and an oxidative addition results in the formation of a Ni(II) alkyliodide complex. The addition of carbon monoxide is followed by an alkyl migration and a subsequent reductive elimination allows the recovery of acetic acid product and regeneration of the carrier.
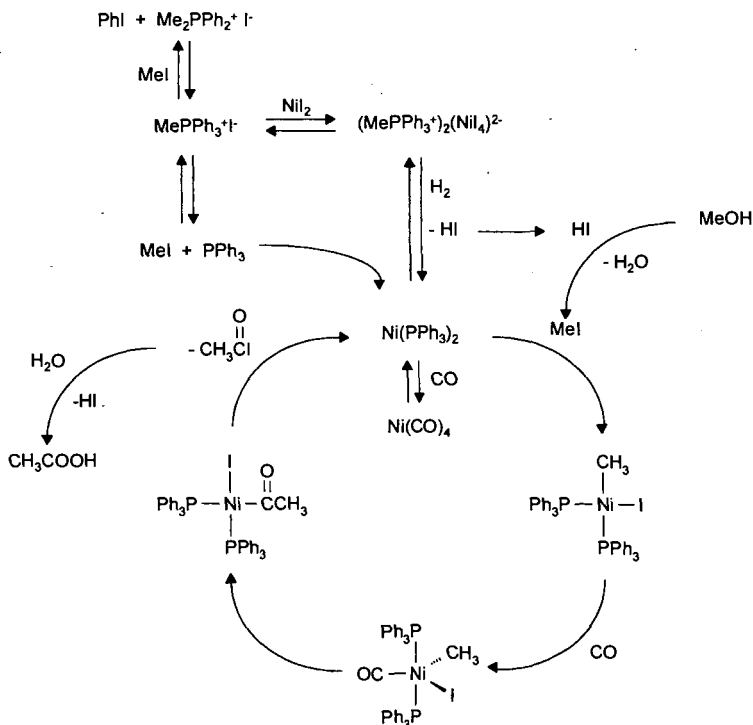

Figure 2: Mechanism of the Nickel Catalyzed Carbonylation of Methanol

CIR-FTIR observations indicate that there is no build-up of nickel carbonyl species during the course of the reaction so that the slow step(s) of the process must occur before the addition of carbon monoxide.

The course of a typical batch reaction, as measured by the uptake of carbon monoxide (Figure 3), can be used to examine catalyst activation. In this particular case one can note a persistent induction period that spans about 40 minutes followed by a period of well-behaved steady-state catalysis and finally the loss of rate associated with depletion of the reactants.
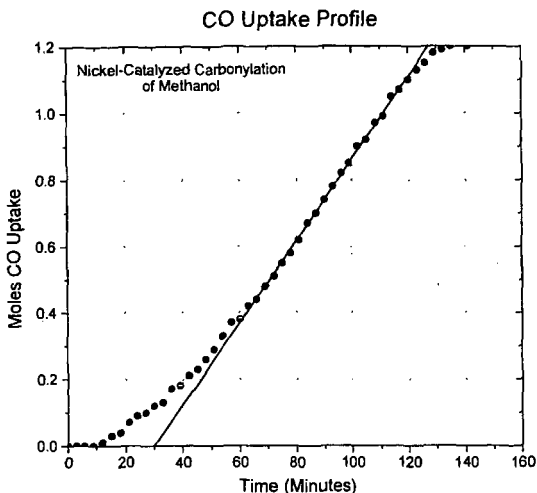
CO Uptake Profile

Figure 3: Course of Typical Batch Reaction

The length of the induction period has been shown to depend upon both the nature of the nickel compound charged to the reactor as well as the partial pressure of hydrogen present in it. With NiI_2, triphenylphosphine and the reaction conditions as indicated in the experimental section the induction period is minimized. However, the details of the reduction process have not yet been elucidated and we cannot distinguish between the direct formation of "NiL_2" or the intermediate formation of $Ni(CO)_4$ which subsequently reacts with free ligand.

The rate of the reaction shows first-order dependence upon the concentration of nickel and methyl iodide. The reaction is also first-order with respect to carbon monoxide at lower pressures. These results are consistent with the CIR-FTIR observations noted above. However, at higher carbon monoxide pressures the rate of reaction is inhibited indicating that is it possible for carbon monoxide to compete effectively with the free ligand present in solution. In fact, as one might predict from this mechanism, higher concentrations of phosphine promoter are required in order to obtain the maximum rate of reaction at higher carbon monoxide partial pressures.

Also consistent with the above mechanism is the observation that the rate of catalysis depends upon the identity of the phosphine promoter used. The identity of the phosphine determines the position of the dissociative equilibrium from the phosphonium iodide and thus the amount of free ligand available as well as the rate of the reaction of the various ligand substituted nickel intermediates. It was shown that both the steric and electronic properties of the phosphine promoters play a role in determining reaction rates.

Conclusions

The mechanism of the phosphine promoted nickel-catalyzed carbonylation of methanol has been shown to involve the equilibrium dissociation of free phosphine from the phosphonium iodide present under reaction conditions. This free phosphine is able to compete effectively as ligand with carbon monoxide in the formation of the catalytically active zero-valent nickel intermediates. The rate of reaction can be favorably influenced by the nature of the phosphine promoter used and under conditions which provide rapid rates for carbonylation $Ni(CO)_4$ is present in only trace quantities.

Acknowledgements

References

[1] W.R. Moser, B.J. Marshik-Guerts, S.J. Okrasinski, J. Molecular Catalysis A: Chemical 143 (1999) 57-69.
[2] W.R. Moser, B.J. Marshik-Guerts, S.J. Okrasinski, J. Molecular Catalysis A: Chemical 143 (1999) 71-83.